



# Synthesis and application of molecularly imprinted silica for the selective extraction of some polar organophosphorus pesticides from almond oil<sup>☆</sup>

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## H I G H L I G H T S

- Screening of the synthesis conditions of MISs for organophosphorus pesticides.
- Optimization of the extraction procedure for the clean-up of almond oil extracts.
- Selective extraction of organophosphorus pesticides from almond oils.
- LOQs obtained for almond lower than the established MRLs.

## A R T I C L E I N F O

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## A B S T R A C T

The aim of this work was to prepare and evaluate molecularly imprinted polymers obtained by a sol-gel approach for the selective solid-phase extraction (SPE) of organophosphorus pesticides (OPs) from almond oil. The performances of molecularly imprinted silicas (MISs), prepared using different conditions of synthesis, were studied by applying different extraction procedures in order to determine the ability of the MISs to selectively extract ten target OPs. For this, the retention of OPs on MISs in pure media was compared with the retention on a non-imprinted silicas (NISs), used as control sorbent, to prove the presence of specific cavities. The most promising MIS allowed the selective extraction of the 3 most polar OPs among the 10 studied. The capacity was studied and the repeatability of the extraction recovery yield was demonstrated both in pure and real media. This MIS was able to selectively extract fenthion sulfoxide and dimethoate contained in almond oil extract after applying the optimized extraction procedure with recovery yields between 100 and 114%. The estimated limit of quantification (LOQ, S/N = 10), thanks to LC/MS analysis in MRM mode, between 1.2 and 4.6 µg/kg for those OPs in the almond fruits, was more than 10 times lower than the Maximum Residue Levels (MRLs) established by the European Commission. This MIS therefore shows a high potential for the analysis of those two polar OPs at trace levels from almond oils.

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## 1. Introduction

Almond oil (*Oleum amygdalae*) provides important health

benefits such as reducing the incidence of obesity, cardiovascular diseases, diabetes or cancer. It is used in many fields in the food or pharmaceutical industries [1]. For instance, it is used to treat dry skin in psoriasis and eczema [2]. It is also largely employed in the cosmetic industry for its penetrating, moisturizing and restructuring properties. However, some pesticides, especially highly lipophilic ones, can be easily bio-accumulated in almond fruits and hence be transferred into the oil during the trituration process [3]. For this reason, the Maximum Residue Level (MRL), which is the highest level of a pesticide residue that is legally tolerated, was

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established by the European Commission to control the presence of these contaminants in raw materials such as oil seeds and fruits. Because MRLs on processed products are not yet established, a processing factor was proposed by FEDIOL (vegetable oil and protein meal industry association) that can be used to evaluate the corresponding contamination level in oils.

This study focused on organophosphorus pesticides (OPs) that are mainly used to protect plants [4]. However, these compounds are known as inhibitors of acetylcholinesterase [5]. OPs have a tendency to bind to this enzyme thus disturbing nerve function, which further results in paralysis and death [6]. Extraction of OPs from oil matrices containing a high content of triglycerides and the possible presence of lipophilic analytes [7] requires complicated sample treatment procedures before chromatographic analysis. In general, OPs are extracted from vegetable oil samples by using liquid-liquid extraction (LLE) [8–10] or low temperature extraction [11] with a clean-up step like gel permeation chromatography (GPC) [12], matrix solid-phase dispersion (MSDP) including QuEChERS [7,8,13,14], or headspace solid-phase microextraction (HS-SPME) [14]. These techniques normally combined with performing chromatographic methods such as GC-MS/MS or LC-MS/MS allow the target analytes, that might be present in low quantities in this kind of sample, to be extracted, identified and quantified. Solid-phase extraction (SPE) [15–17] is also still largely used as an extraction technique of OPs from oils. Nevertheless, conventional sorbents (such as Florisil, alumina or silica) that favor polar interactions in apolar matrices such as oils can also lead to the co-extraction of numerous interfering compounds. In order to decrease the incidence of this phenomenon and to increase selectivity of the sample treatment, molecularly imprinted polymers (MIPs) can be used as selective sorbents since they possess specific recognition sites based on the molecular recognition of the target OPs. Indeed, they contain specific recognition sites that are sterically and chemically complementary to the template molecule, thus allowing the latter to be selectively recognized in real samples [18–21].

MIPs were applied as SPE sorbents [19,20,22–24] but also in other extraction techniques such as MSPD [23,24], dispersive solid phase extraction [25,26], SPME [27] or stir bar sorption extraction [28] to selectively extract OPs from several samples such as fruits [19,20,22–24], soils [25,26] or vegetables [25,26]. To date, few studies reported the use of MIPs for the selective extraction of OPs in vegetable oils [29–32]. Among these studies, one described the synthesis and the characterization of a MIP that target the dimethoate and some structural analogs. The resulting MIP was able to extract selectively a single OP, the dimethoate from pure media (with recovery of 70% on MIP and of only 21% on NIP -non imprinted polymer-) but the selectivity was not proven in real media [32]. Otherwise, three studies of Bakas et al. have reported the selective extraction using MIP sorbents in SPE focusing on a single OP from olive oil in each study, *i.e.* methidathion [29], dimethoate [30] and fenthion [31]. To date, only one work, previously reported by our group, showed the possibility to extract several OPs simultaneously from oil [33]. Indeed, after screening different conditions of synthesis, a MIP was selected for its capacity to extract selectively three OPs. After optimizing the extraction procedure, three moderately polar OPs among the studied OPs were successfully selectively extracted (methidathion, malathion and diazinon). As OPs belong to a wide range of structures and of polarities, it was complicated to trap the whole family of OPs. In order to selectively extract OPs with a different structure and/or physico-chemicals properties, as alternative to radical polymerization, imprinted sorbent produced by a sol gel *i.e.* molecularly imprinted silica (MIS) sorbents were proposed in this work.

MISs are generally synthesized by using 3-aminopropyl

triethoxysilane (APTES) or phenyltriethoxysilane (PTMOS) (having respectively an amino or a phenyl group) as monomers that led to the formation of polar (hydrogen bonds, electrostatic interactions), hydrophobic and  $\pi$ - $\pi$  interactions depending of the monomer and of the solvent used. The cross-linking agent is an alkoxy silane, *i.e.* tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) [34]. The synthesis of MISs is similar to those of MIPs. First the monomer and the cross-linker reacts mainly in aqueous solution to form silanol (Si-OH) groups through hydrolysis, then siloxane bonds (Si-O-Si) are formed by condensation reaction with the silanol groups around the template molecule with the help of an acidic or a basic catalyst [34]. The pH of the mixture will determine whether the dominant process is hydrolysis or condensation. The use of an acidic catalyst results in a slow hydrolysis step and a rapid condensation, the growth of the “polymer” being favored in comparison with the cross-linking. The polymer formed is then rather homogeneous, with small pores and a large specific surface area. Conversely, when a basic catalyst is used, the hydrolysis becomes the fast step and the condensation is the slow one. In this case, the polymer chain will rapidly cross-link and form particles that lead to a heterogeneous structure, obtained more rapidly than in acid catalysis. In these conditions, the specific surface area is smaller and the pores are larger, so the density of the “polymer” in basic catalysis will be lower [35,36]. Sol gel reactions not only depend on the pH of the solution and the type of catalyst, they also depend on the temperature of the reaction, heating time or the solvent [37]. This sol gel technique was applied to the synthesis of MISs for SPME fibers using parathion ethyl [38] or diazinon [39] as template. These SPME fibers were used to extract templates and their structural analogs from aqueous matrices like fruits [38] or vegetable extracts [39]. This approach was also used for the synthesis of electrochemical sensors that exhibited a good selectivity in liquid phase for the parathion in pure media [40] or in real samples (rice) [41]. MISs have been used as SPE selective sorbents for different compounds such as a neurotoxic non-proteinogenic amino acid ( $\beta$ -N-methylamino-L-alanine) from cyanobacterial samples [42], nitroaromatic explosives from post-blast samples [34] or ibuprofen from urine [35] but never for the OPs.

This work describes for the first time the synthesis of MISs for the extraction of OPs from almond oil. The targeted OPs were selected by taking into account the risk of their occurrence in such samples. Different conditions of synthesis were screened by varying the nature of the template, the monomer and the porogenic solvent. After this screening, the most promising MIS in terms of retention and selectivity was studied in more detail by investigating its behavior towards ten OPs in pure media. The repeatability of the molecularly imprinted solid-phase extraction (MISPE) procedure was demonstrated for a selection of compounds and the capacity was studied. Finally, in order to selectively extract some OPs at trace levels in almond oil, the extraction procedure was optimized. After this optimization, the matrix effect occurring during LC-MS/MS analysis were studied and the limits of detection and quantification were determined and compared with the MRLs established by the European Commission.

## 2. Materials and methods

### 2.1. Chemicals

Organophosphorus (OPs) standards: dimethoate (DMT) 98%, fenthion sulfoxide (FSX) 99%, fenthion sulfone (FSN) 99%, methidathion (MTH) 98%, malathion (MAL) 99%, fenitrothion (FNT) 98%, diazinon (DIZ) 98%, pirimiphos-methyl (PIM) 99.5%, fenthion (FEN) 99% and chlorpyrifos-ethyl (CLE) 99.5% were supplied by Cluzeau Info Labo (Sainte-Foy-La-Grande, France). Individual stock

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